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(54) **Method and apparatus for analysis of particulate content of gases**

(57) Method of analysis of particulate content of gases, applicable to the quantitative and qualitative analysis of vehicle engine emissions and otherwise comprises sampling, removing particles and analysis of the removed particles. Sampling is effected by electro-static precipitation using a catalyst-coated piezo-electric crystal. The analysis of the removed particles is effected by heating the crystal in an oxidising atmosphere to oxi-dise the deposited particles. Connection of the crystal to an oscillation circuit enables the frequency of oscillation of the crystal to be monitored. Changes in the frequency of oscillation are interpreted to provide quantitative and qualitative analysis of particles deposited and subse-quently oxidised.

Fig 2.
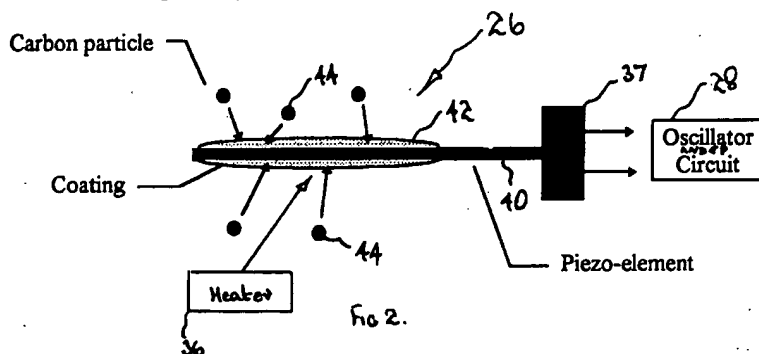
EP 0 779 510 A2

Description

FIELD OF THE INVENTION

This invention relates to a method and apparatus for analysis of particulate content of gases. An example of the application of the invention is to the qualitative and quantitative analysis of emissions from internal combustion engines, particularly vehicle engines, but the invention is applicable also more widely than in the automotive field.

BACKGROUND OF THE INVENTION

The analysis of particulate matter in air and other gases is performed in a wide variety of industries and applications. In the automotive sector, exhaust emissions from automobiles and cars and trucks and lorries are measured during and post manufacture and in the aftermarket to ensure compliance with increasingly restrictive official regulations. The particulate matter (soot) generated by diesel engines is a focus for legislative control and is at present the subject of studies into its effects on public health. It is likely that supplementary regulations relating to the particulate content in vehicle emissions will compel automotive and other manufacturers to investigate the means to reduce such levels in original equipment. Likewise, ensuring compliance of engines in use in the aftermarket may entail a modification to the tests carried out on a compulsory basis in many countries to determine compliance with official requirements.

Currently available equipment for determination of particulate content of engine emissions, as used in Europe in the aftermarket, is based upon the measurement of opacity using a comparatively simple and inexpensive instrument. Another technique uses a volumetrically-controlled sample of engine emission gas which is drawn through a filter element and the degrees of discolouration of the filter element is used as an index for the amount of soot emitted. Both these techniques are unsuitable for the quantitative analysis of sub-micron particles and provide no qualitative information, as such, at all.

As regards engine emission tests carried out during and after engine manufacture, these are more complex. Exhaust emissions are tested on a chassis dynameter or engine test stand using the CVS (controlled volume sampling) method. In this method, the exhaust gases are diluted with filtered ambient air and extracted with a blower and applied to a standardised test procedure. The dilution inhibits condensation and agglomeration effects during sample collection. Dilution also holds the sample temperature at the level required for particulate measurement. Several techniques are available for particulate measurement, including gravimetric measurement, differential mobility analysis and condensation core counting. At present, the gravimetric technique is the most widely used means of assessment, but it lacks

sensitivity at low particulate levels and measurement time is lengthy. All these available techniques involve relatively large and expensive equipment, which arises particularly as a result of the use of the dilution system, which simulates the physical and chemical processes which the particulate emissions undergo in the atmosphere.

As to laboratory techniques for particulate measurement, many methods have been developed including the use of the quartz crystal microbalance and the electrostatic precipitator. To the best of the Applicant's knowledge these techniques have not been applied to the qualitative and/or quantitative analysis of automotive emissions and the like.

There is disclosed in US 3,478,573 (King) a piezoelectric crystal having an integral heater and suitable for use in measuring devices such as gas analysers. An electronic oscillator is controlled by the piezoelectric material. A coating on the piezoelectric material is adapted to interact with at least one component of a fluid to be analysed and the resulting changes in the frequency of the piezoelectric material as it interacts with the fluid are monitored for analytical purposes. The process is subject to the limitations evident from the development of the present invention including inferior sensitivity and less clear-cut simplicity of construction as compared with the analytical desorbtion process of the embodiments of the present invention.

There is disclosed in US 5,056,355 (Hepher) a device for monitoring dust or other particulate material in gas and comprising the use of a piezoelectric sensor and the step of monitoring variations in the resonant frequency of the sensor as induced by the aggregation of dust on the sensor. The system of this prior proposal is likewise subject to the limitation highlighted by the embodiments of the present invention and arising from the use of a technique in which the frequency monitoring step is applied to the process of particulate aggregation or addition to the sensor, as opposed to the converse system employed in the embodiments of the invention.

GB-A-2 270 564 (GEC Marconi) discloses a method of identifying fluid materials or analytes using a piezoelectric crystal oscillator. The system operates on the basis of monitoring a step change in the concentration of the analyte, leading to a characteristic frequency change enabling identification of the analyte. The method includes an embodiment using a reverse step in concentration change. However, this disclosure in common with the other prior proposals known to the Applicants lacks any suggestion of the technical merit of monitoring the frequency change resulting from the inverse step of particulate desorbtion or removal from the piezoelectric substrate, with its attendant advantanges as disclosed herein.

US patents

3,561,253
4,561,286

4,041,768

4,446,720

all disclose particulate mass measurement systems which monitor frequency changes in oscillating piezoe-lectric devices on which particulate matter is deposited, such as by electrostatic deposition, but none of these discloses or suggests a system in which the technical benefits of applying the analytical step to a process for the removal, partial or complete, of the particulate mat-ter from the piezoelectric substrate, nor indeed a proc-ess by which such an inverse step could be accomplished in a piezoelectric device while monitoring frequency changes. It is believed to be novel to utilise a piezoelectric crystal device as a basis for performing (on a frequency basis) a process of thermogravimetric analysis of the particulate content of a gas sample. The piezoelectric crystal permits gravimetric monitoring of the process of thermal (oxidative, or otherwise chemi-cally) removal of particulate material deposited thereon. The use of this removal or desorbtion step as the basis for analysis means that a thermo-gravimetric basis for analysis (which is novel in relation to piezoelectric devices) can be utilised, which enables frequency pro-file analysis to be performed, both in relation to particu-late size and particulate identity.

The disclosure in US 5,056,355 is taken as the basis for the two-part form of claim 1 hereof.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method and apparatus, particularly but not exclusively applicable to the qualitative and/or quantitative analysis of automotive emissions, providing improvements in relation to currently available equipment, notably in rela-tion to compactness of the apparatus and/or simplicity or speed of the method and/or cost of the apparatus and/or the method, or other improvements disclosed herein or generally.

According to the invention a method and apparatus for the analysis of particulate content of gases com-prises the steps of sampling the gas, removing particles from the gas sample, and subjecting the removed parti-cles to analysis.

In accordance with the invention, the step of removal of the particles from the gas sample comprises causing the particles to be deposited on a substrate. Further in accordance with the invention, the step of analysis comprises causing at least some of the depos-ited particles to be removed from the substrate and the application of a measurement technique to this step of removal in order to determine qualitative or quantitative information concerning the particulate content of the gas to be analysed.

The steps of sampling and removal and analysis correspond to steps of analysis known from the use of an electrostatic precipitator. By the additional steps of causing the particles to be deposited on a substrate and

some at least of these to be subsequently removed while analysis takes place, in accordance with the invention, enables a simple and rapid determination of information concerning the qualitative and/or quantita-tive content of the gas to be analysed, thereby reducing the need for subsequent flushing or cleaning before repeat use.

Thus, in one embodiment, the step of removal of the particles is carried out by means of a electrostatic precipitation technique employing a metal-coated piezo-electric crystal forming an anode in the precipita-tion step. Then, some at least of the particles deposited on the electrode are removed in an oxidising step merely by application of heat and an oxidising atmos-phere to the piezo-electric crystal so that qualitative and quantitative information can be obtained concerning the particles deposited.

This is achieved by connecting the electrode to an oscillator circuit and monitoring the changes in the fre-quency of oscillation as the particles are initially depos-ited and subsequently removed. Interpretation of the profile of the graph of rate of change of mass of the electrode provides a basis for determining the identity and/or quantitative presence of materials deposited and removed from the electrode.

Accordingly, the embodiments of the invention pro-vide a method and apparatus whereby a relatively sim-ple item of electrical equipment can obtain both qualitative and quantitative data relating to particulate content of gases on a relatively rapid basis.

While the principal applications of the invention are expected to be in the testing of automobile exhaust emissions, both at the time of manufacture and in the automotive aftermarket, it is expected that a variant of the embodiments could be developed for environmental or industrial pollution monitoring.

Embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which :

Fig 1 shows in block diagram form an embodiment of apparatus according to the invention;
Fig 2 shows an elevation view of an electrode form-ing part of the apparatus of Fig 1; and
Fig 3 shows a plot of mass against time for a part of the process carried out by the apparatus of Figs 1 and 2, relating to removal of particles from the elec-trode of Fig 2.

As shown in the drawings, apparatus 10 for analy-sis for particulate content of gases comprises sensor elements 12, 14, a multiplexer 16, a data capture sys-tem 18, signal processing apparatus 20 together with data storage means 22 and gas analysis

output means 24. These general elements of the apparatus will now be described in more detail.

Sensor elements 12 and 14 represent two of an optional range of elements for analysis of a variety of gases. Each sensor element comprises an electrode 26

as shown in Fig 2 coupled to an oscillator and electrostatic precipitator circuit 28.

Each sensor element 12, 14 has electrode 26 mounted within a glass envelope indicated at 30, 32 in Fig 1 to which a gas to be analysed is supplied by sampling means 34.

Sampling means 34 comprises known apparatus for extracting a volumetrically controlled sample from a gas supply and adapted to deliver same to envelopes 30, 32 containing electrodes 26.

The electrode 26 and the associated electrostatic precipitation circuit 28 constitute removal means adapted to remove particles from the gas sample delivered to envelope 30 or 32 by sampling means 34. The electrode performs the removal step by electrostatic precipitation. It will also be understood that the removal means 26 and 28 also constitute deposition means adapted to deposit the particles on a substrate constituted by the electrode 26.

Further in relation to terminology employed in the definition of the present invention, there is provided further removal means adapted to remove deposited particles from the substrate or electrode 26, and such further removal means is constituted by a heater 36 which effects such removal in combination with oxidation gas supply means 38 which is adapted to supply an oxidising gas mixture to the envelopes 30, 32 for a purpose to be more fully described below, in a manner analogous to sampling means 36.

Finally, it will be understood that circuits 16, 18, 20 and 22 provide a measurement function in relation to sensor elements 12 and 14 enabling measurement of the step of removal of particles from electrode 26 by the above-mentioned oxidation step for the determination of the particulate content of a gas being analysed.

Turning now to a more detailed description of the above-mentioned main features of the apparatus 10, sensor elements 12 and 14 will now be more fully described with reference to Figs 1 and 2.

Sensor elements 12 and 14 comprise electrodes 26 as shown in Fig 2 mounted at 37, respectively, in envelopes 30, 32 which are connected to sampling means 34 and the oxidation gas supply means 38. Electrode 26 is in the form of a piezoelectric crystal comprising an AT-cut 10 megahertz crystal 40 having gold-plated electrodes and connected to oscillator circuit 28. Crystal 40 has a coating 42 of a catalytic metal eg platinum or antimony and forms the anode in the electrostatic precipitator circuit 28. In use, electrode 26 causes particulate matter (shown diagrammatically at 44) to become charged and to move towards and adhere to crystal 40. Crystal 40 becomes loaded with the particulate matter to an extent that reflects the particulate density in the gas mixture to be analysed. This mass loading of the crystal 40 produces a measurable negative shift (reduction) in the oscillation frequency of crystal 40 in association with oscillator circuit 28. A frequency shift of the order of some hundreds of hertz can be expected.

Turning to Fig 1 of the drawings, it will be seen that

sensor elements 12 and 14 are shown connected to multiplexer 16. The multiplexer and following data processing stages 18, 20 and 22 are adapted to receive frequency information from electrode 26. For simplicity of illustration in Fig 1, the oscillator and electrostatic precipitator circuits 28 seen in Fig 2 are not shown. It is to be understood that, of course, these circuits remain in operational connection to electrode 26 in accordance with the requirements of the analysis process described herein.

Turning now to the general mode of operation of apparatus 10, this is as follows. Sampling means 34 delivers the gas to be analysed to envelopes 30, 32 and thus to the electrodes 26 therein. These effect an electrostatic deposition of particulate content of the gas samples onto the material of the electrode where it is captured by the catalytic coating 42. Sampling means 34 comprises a pump for gas delivery purposes. It is believed that the construction and operation of the oscillator and electrostatic precipitator circuit 28 will be well known to those skilled in the technical field and therefore these are not further described here.

Oscillator circuit 28 is activated to establish a preliminary oscillation frequency prior to the electrostatic deposition stage. Then the electrostatic precipitator circuit is energised to effect such precipitation, whereupon there is a frequency shift as described above, in accordance with the mass of particulate deposited.

After this deposition step in relation to particulate matter from the gas sample, there follows the step of removal of the particulate from the electrodes 26. This is effected by activating the supply 38 of oxididation gas so that the gas to be sampled is flushed out and electrode 26 is surrounded by an oxidising atmosphere. Thereupon heater 36 is energised. The heater may, for example, be a laser beam, focused upon the electrode whereby the deposited particles are caused to be removed from the electrode by oxidation in the elevated temperature and oxidising atmosphere conditions thus-provided.

During this process of particulate removal from the electrode 26, the oscillation frequency of electrodes 26 and oscillator circuit 28 continue to be monitored by the data-processing system 16, 18, 20 and 22. The resultant shift in oscillation frequency occurring in such a situation is shown, for one typical example, in Fig 3 where the mass of material deposited is plotted against time. This plot is obtained during the oxidation step since mass can be seen here to reduce substantially with time.

As the particulate material mass loading on crystals 40 reduces, the oscillation frequency correspondingly increases. The graphic presentation in Fig 3 is derived from the frequency shift information provided to the data handling system, 16, 18, 20 and 22. The profile of the plot 46 enables interpretation of the presence of particulates on a qualitative basis. For example, the dip shown at 48 in Fig 3 corresponds to the removal of the soluble organic fraction (SOF) from the electrode. The

features of the plot identified at 50 are characteristic of the break-up of particulate content. The method permits analysis of the agglomeration (total mass of material deposited and its removal), and the sulphate content and the soluble organic fraction. The shape of the curve at location 50 is characteristic of the break-up of agglomerated particulate matter.

After use, flushing or de-gasing of the sensor elements 12 and 14 can be accomplished by reversing the pularity of the precipitator and flushing the envelopes 30, 32 with nitrogen.

In the above embodiment, the sensor elements 30 and 32 may be provided with specific abilities to absorb and permit analysis of specific hydrocarbons, or a family of hydrocarbons, by varying the material of the coating on the electrode. Accordingly, if so required, an array of similar piezoelectric electrodes 26 may be provided in order to deal with the analysis of particular gas constituents. Such provision is indicated at 50 in Fig 1.

In Fig 3 the alternative curve dip profiles shown at 52 and 54 enable interpretation of specific constituent materials in the same manner as the profiles shown at 48 and 50, and notably in relation to the particle size of an identified constituent, the dip profiles 52, 54, 56 each being characteristic of a range of particle sizes. Such interpretation is effected by the data processing apparatus shown in Fig 1 namely multiplexer 16, data capture system 18, signal processing system and data storage system 22, on the basis of prior test work using known gas samples, of known particle size.

In a further embodiment, there may be employed a chromatagraph (not shown) in association with the thermographic analysis apparatus described above, in order to provide additional data in relation to the analysis of the gas in question.

Claims

1. A method of analysis of particulate content of gases comprising :

   a) sampling a gas to be analysed;
   b) removing particles from said sample;
   c) subjecting said removed particles to analysis; and
   d) said step of removing said particles comprising causing said particles to be deposited on a frequency-responsive substrate;
      characterised by
   e) said step of analysis comprising causing at least some of said deposited particles to be at least partially removed from said frequency-responsive substrate; and
   f) said step of analysis further comprising applying a frequency monitoring technique to said step of at least partial removal of said particles from said substrate in order to determine information concerning the particulate content of said gas to be analysed.

2. A method of analysis of particulate content of gases characterised by the step of at least partially removing from a substrate particles deposited from a gas sample and the method comprising applying a measurement technique to said step of removal of particles from said substrate so as to determine information concerning the particulate content of said gas to be analysed.

3. A method according to claim 1 characterised by said step of removing particles from said sample of gas to be analysed comprising causing electrostatic precipitation of said particles on said substrate.

4. A method according to claim 3 characterised by said electrostatic precipitation comprising precipitating said particles on said frequency responsive substrate comprising a metal-coated piezo-electric crystal forming an anode in said precipitation step.

5. A method according to claim 4 characterised by employing as said metal coating on said anode a catalytic metal.

6. A method according to any one of the preceding claims characterised by said step of removal of said particles from said frequency responsive substrate comprising oxidising said particles by heating said substrate in an oxidising atmosphere.

7. A method according to claim 6 characterised by said step of applying a frequency monitoring technique to said step of removal of said particles from said substrate comprising employing said substrate as an electrode in an electrostatic precipitator circuit and connecting said electrode to an oscillator circuit and determining the frequency of oscillation as a measure of the mass of particles remaining on said substrate, as said oxidation proceeds.

8. A method according to claim 7 characterised by said step of determining the frequency of oscillation comprising monitoring changes in the oscillation frequency of said circuit as said measure of the mass of the particles remaining on said substrate.

9. A method according to claim 8 characterised by said step of applying a frequency monitoring technique comprising determining changes in the gradient or profile of the graph of the rate of change of mass of said substrate as a basis for determining the identity and/or particle size of particulate materials deposited and removed from said substrate.

10. Apparatus for the analysis of particulate content of gases comprising :

    a) sampling means adapted to sample a gas to

be analysed;

b) removal means adapted to remove particles from said sample;

c) analysis means adapted to analyse said particles removed from said sample; and

d) deposition means adapted to deposit said particles on a frequency-responsive substrate; characterised by

e) further removal means adapted to remove at least partially at least some of said deposited particles from said substrate; and

f) frequency monitoring measurement means adapted to measure one or more aspects of said step of at least partial removal of said particles from said substrate in order to determine information concerning the particulate content of said gas to be analysed.

11. Apparatus for the analysis of particulate content of gases comprising a substrate adapted to receive particles to be deposited thereon from a sample of said gas to be analysed, and removal means adapted to remove at least partially at least some of said deposited particles to permit measurement means to determine information concerning the particulate content of said gas to be analysed on the basis of said removal step.

12. Apparatus according to claim 10 characterised by said first removal means for removing particles from said gas sample comprising electrostatic precipitation apparatus.

13. Apparatus according to claim 12 characterised by said electrostatic precipitation apparatus comprising a metal-coated piezo-electric crystal forming an anode in said electro static precipitation apparatus.

14. Apparatus according to claim 13 characterised by said metallic coating of said anode comprising a catalytic metal.

15. Apparatus according to any one of claims 10 to 14 characterised by said further removal means being adapted to remove at least some of said particles from said frequency responsive substrate comprising heating means for said substrate and gas supply means adapted to supply an oxidising atmosphere to said apparatus whereby said particles thereon can be heated in an oxidising atmosphere to effect oxidisation thereof.

16. Apparatus according to claim 14 characterised by said frequency responsive measurement means adapted to measure an aspect of the step of removal of said particles from said substrate comprising an oscillator circuit and said substrate forming an electrode connected as an anode to said oscillator circuit, and frequency measurement

means being provided to determine the frequency of oscillation of said circuit as a measure of the mass of particles remaining on said substrate as said oxidation proceeds.

17. Apparatus according to claim 16 characterised by the step of employing frequency monitoring means to monitor changes in the oscillation frequency as said measure of the mass of particles deposited.

18. Apparatus according to claim 17 characterised by frequency interpretation means adapted to interpret the data obtained by said monitoring step to determine changes in the gradient or profile of said graph of rate of change of mass of said substrate as a basis for determining the identity and/or quantitative presence and/or particle size of materials deposited and removed from said substrate.
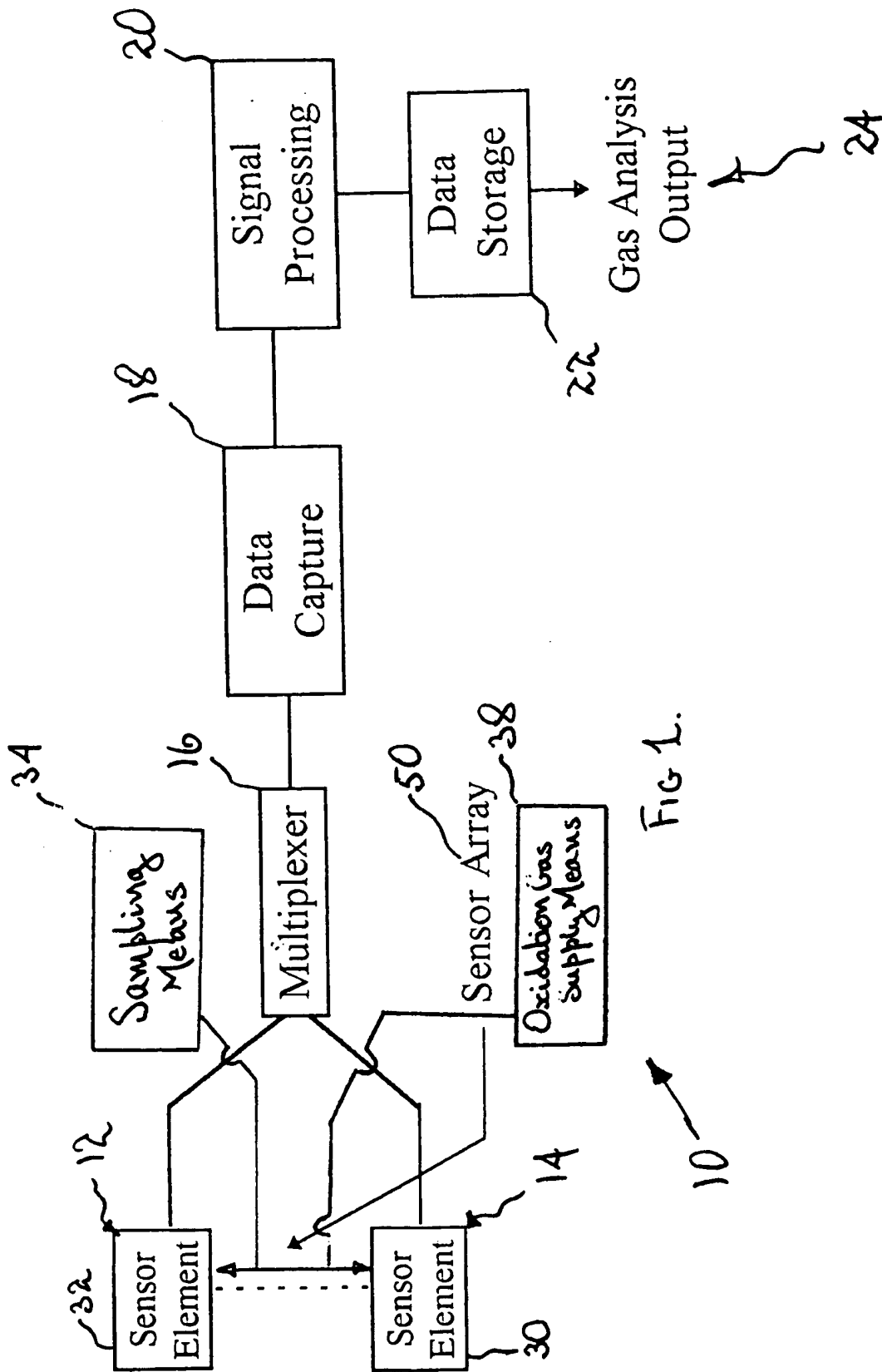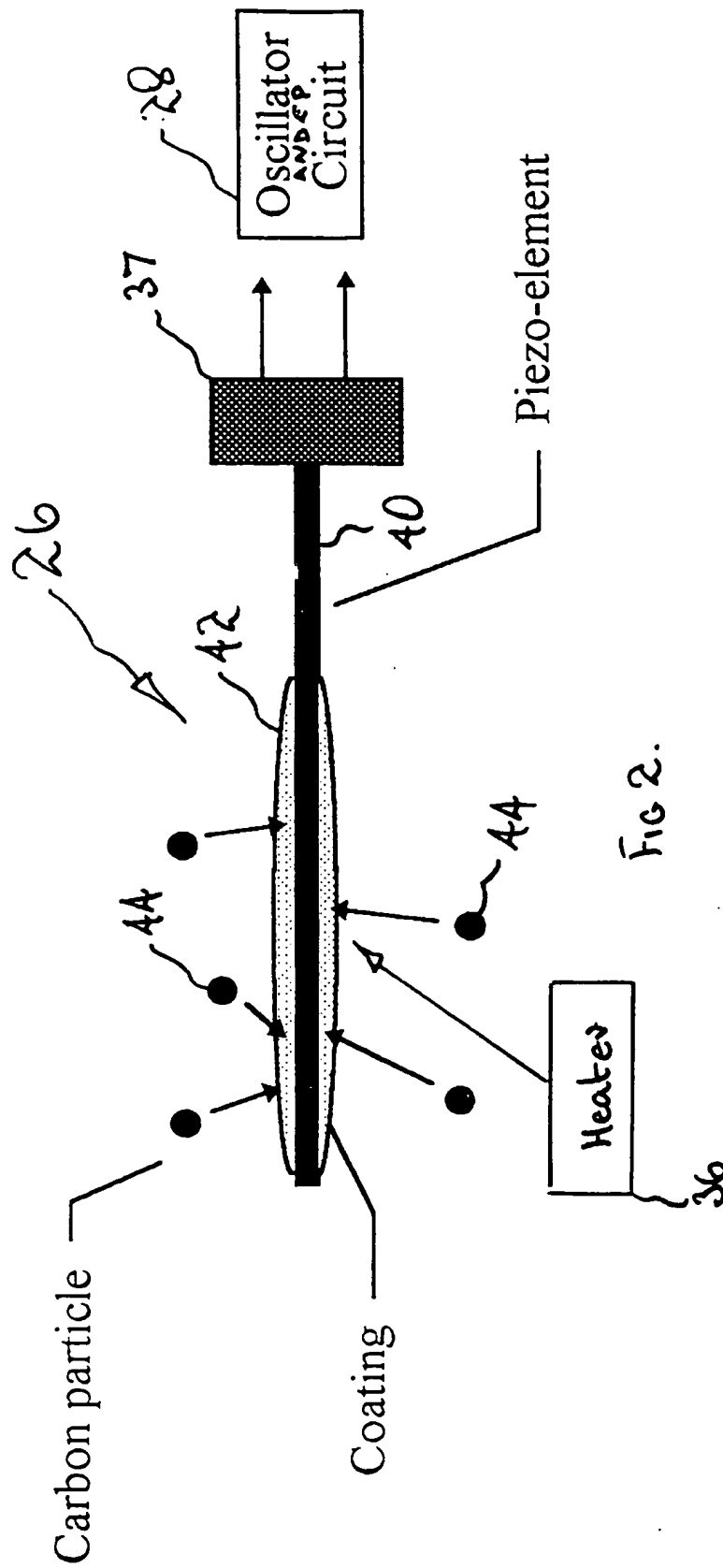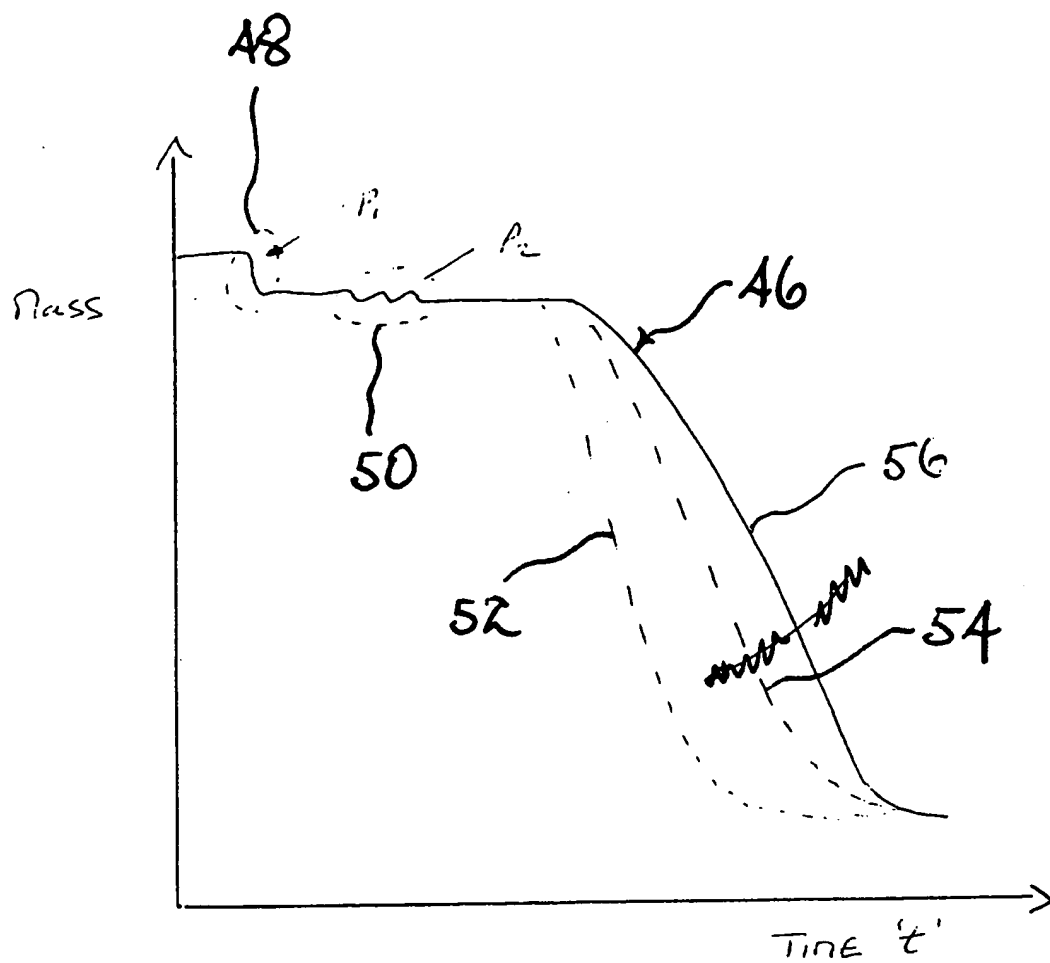
Fig 1.

Fig 2.

Fig 3